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OFFICE OF NAVAL RESEARCH
FIFTEENTH PERIODIC AND FINAL REPORT

for

Contract N00014-77-G-0006

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Fifteenth Periodic and Final Report

to

United States Navy Office of Naval Research

on

ONR Contract No. N00014-77-G-006

Report on period 1st April 1987 - 30th September 1987
and final report of progress made throughout the contract

P.J. Hendra
M. Fleischmann
A. Bewick

March 1988

A. Introduction

Continuing support by O.N.R. has enabled the Southampton group to continue and develop their efforts in three areas in which they might make a claim to have been pioneers - the *in situ* vibrational spectroscopic study of electrode-electrolyte interfaces, detailed investigations of ultra microelectrodes and the structure and properties of polymers rapidly solidified from their melts.

In the report given below we briefly outline progress laying the heaviest emphasis on the newest results. For a more detailed coverage of the progress made readers are referred to progress reports 14 and earlier.

B. Vibrational Spectroscopic Studies on Electrode-Electrolyte Interfaces

Raman Spectroscopy of Electrode-Electrolyte Interfaces

We have already reported (31/03/1987) that we have succeeded in obtaining enhanced Raman spectra from the interfaces between metal overlayers (deposited on SERS active substrates) and electrolyte solutions. The papers dealing with Pb, Tl, Zu, Ni, CO and Cu on Ag substrates have now appeared in print:

M. Fleischmann and Z.Q. Tian, The Effects of the Underpotential and Overpotential Deposition and Lead and Thallium on Silver on the Raman Spectra of Adsorbates, J. Electroanal. Chem. 217 (1987) 385.

M. Fleischmann, Z.Q. Tian and L.J. Li, Raman Spectroscopy of Adsorbates on Thin Film Electrodes Deposited on Silver Substrates, J. Electroanal Chem., 217 (1987) 397.

M. Fleischmann and Z.Q. Tian, The Induction of SERS on Smooth Ag by the Deposition of Ni and CO, J. electroanal. Chem., 217 (1987) 411.

The paper dealing with Fe:

G. Mengoli, M.M. Musiani, M. Fleischmann, B.W. Mao and Z.Q. Tian, Enhanced Raman Scattering from Iron Electrodes, Electrochim. Acta

still in press.

A paper dealing with the interpretation of the spectra of octahedral ions adsorbed at metal electrodes has been published in association with the groups of Professor S. Pons (Salt Lake City, Utah) and Professor P.P. Schmidt (Oakland Michigan):

S. Pons and M. Fleischmann, Theoretical Analysis of the Vibrational Spectra of Ferricyanide and Ferrocyanide Adsorbed on Metal Electrodes, J. Phys. Chem., 91 (1987) 5568.

The major new development has been the observation of Near Infra Red Fourier Transform Enhanced Spectra (NIFTERS) from silver electrodes. The signal intensities already achieved are comparable to the highest intensities which have been obtained for solid samples using near I.R. fourier Transform Raman techniques. We believe that NIFTERS will prove to be the method of choice for the measurement of Raman spectra at electrode-solution interfaces.

X-Ray Diffraction at Electrode Surfaces

The investigation of platinum-solution interfaces (covering changes in structure due to changes in the double layer potential, oxide formation, the adsorption of 'weakly adsorbed' hydrogen and the adsorption of carbon monoxide) has now appeared in print:

M. Fleischmann and B.W. Mao, In-situ X-Ray Diffraction Studies of Pt Electrode-Solution Interfaces, J. Electroanal. Chem, 229 (1987) 125.

It has become apparent that the structural changes induced by the adsorption of hydrogen could be assigned to the restructuring of (110) facets, an interpretation more closely in line with the electrochemical behaviour than the original explanation. A short note on this topic has been accepted for publication:

Microelectrode Research

The investigation of the behaviour of systems in polar solvents in the absence of support electrolytes and of measurements in solvents of low dielectric constant in the presence of electrolytes has now appeared in print:

M.J. Peria, M. Fleischmann and N. Garrard, Voltammetric Measurements with Microelectrodes in Low Conductivity Systems, J. Electroanal. Chem., 220 (1987) 31.

A paper on the in situ determination of low concentrations of lead in battery systems has been published:

L.J. Li, M. Fleischmann and L. Peter, In-situ Measurements of Pb^{2+} Concentration in the Lead-Acid Battery using Mercury Ultramicroelectrodes, Electrochim. Acta, 32 (1987) 1585.

The collaboration with Professor Pons' group on the development of research in this field has continued. The behaviour of microring and microdisc electrodes has been reexamined:

M. Fleischmann and S. Pons, The Behaviour of Microring and Microdisk Electrodes, J. Electroanal. Chem., 232 (1987) 107.

and time dependent processes (and other topics) at microdisc electrodes have been discussed in some detail:

M. Fleischmann and S. Pons, Selected Theoretical Topics in (Eds) M. Fleischmann, S. Pons, D.R. Rolison and P.P. Schmidt, Ultramicroelectrodes, Datatech Systems Inc., Morganton N.C. 28655 - 0435 (1987) 17.

A new form of dropping mercury ultramicroelectrode has been devised; the spherical geometry of this electrode greatly simplifies the mathematical analysis of electrode processes (as compared to the use of disc or ring electrodes) and, indeed, the solutions of many problems have already been given in the literature (although for very different conditions than those which apply to the electrodes of very small size). A first paper on this topic has been accepted for publication in the Journal of Electroanalytical Chemistry.

M. Fleischmann and B.W. Mao, In-situ X-ray diffraction measurements of the surface structure of Pt in the presence of 'weakly' adsorbed H, J. Electroanal. Chem., in the press.

We have been able to demonstrate for the first time that compressed commensurate monolayers of Tl can be formed on Ag both by underpotential deposition and by the interconversion of Tl and Tl I monolayers. The formation of a second incommensurate layer and of highly ordered overpotential deposits has also been monitored. A paper covering this study and dealing also with related measurements for Pb and the deposition on Au electrodes (including the theoretical interpretation of diffraction intensities from two-dimensional arrays) has been accepted for publication:

M. Fleischmann and B. Mao, In-situ X-ray diffraction investigations of the UPD of Tl and Pb on Ag and Au electrodes, J. Electroanal. Chem., in the press.

Structural changes induced in polyaniline films deposited on metal electrodes (the leuco emeraldine-emeraldine transition and the behaviour of iodine doped films) have been investigated and a paper on this subject has been submitted for publication:

M. Fleischmann, N. Garrard, B.W. Mao and G. Mengoli, J. Electroanal. Chem.

The study of electrode solution interfaces by in-situ methods has been reviewed and this paper has now been published:

M. Fleischmann, The Investigation of Electrode-solution Interfaces by in-situ Methods.
The Robert A. Welch Foundation conferences on Chemical Research XXX. Advances in Electrochemistry (1987) 91.

Much of the instrumentation has been redesigned during the present period in preparation for the initiation of a new range of investigations.

Work on electrocrystallisation processes has continued. Investigations of nucleation are referred to in the next section.

Stochastic Processes

The major effort during this period has been the study of electrocrystallisation processes on microelectrodes and especially of those reactions which are important to the operation of the lead-acid battery. By using a sufficiently small substrate it is possible to restrict nucleation to that of a single growth centre (an even smaller microelectrode) which greatly simplifies the interpretation of the data. The arrival time distributions of the first nucleus (in ensembles of repeated experiments) is determined by the kinetics of formation of the first nucleus i.e. we have access to the kinetics of formation of a microelectrode of molecular dimensions. Details of this work were reported at the Elecrochemical Society Meeting in Philadelphia, May 1987 and in a paper presented at the Second Workshop in Interface Phenomena, Compobellow International Park, August 1987 which is due to be published by Springer Verlag:

M. Fleischmann, Electrochemical Processes in Small Systems, in the press.

This paper also contains a short survey of the application of in-situ techniques. Full details of the work on electrocrystallisation and especially that on nucleation are contained in two papers which will be submitted shortly for publication.

The papers on pore formation in lipid bilayers referred to in the last report are also attached.

Infrared Studies

Interest has continued on electrochemical studies on identified crystal faces. Thus, an investigation has been completed on the oxidation of formic acid over Pt(100) + Pt(111) surfaces both in-situ in sulphuric acid as electrolyte-

S.G. Sun, H. Halavikir and A. Bewick, J. Electroanal. Chem. (in press).

Whilst an extension to formaldehyde in alkaline supporting electrolytes using EMIRS has also been presented for publication M. Aurinac-Ivie, R.R. Adjic, A. Bewick and M. Razaq, J. Electroanal. Chem. (in press).

The use of isotopic mixtures is frequently invaluable in explaining EMIRS and related spectra and an example of this approach is also available which serves to define the state or progress at this time. The system involved was CO and Pt

A. Bewick, M. Razaq and J.W. Russell, J. Electroanal. Chem. (in press).

Studies on electrode surfaces using infrared methods have been considerably extended at Southampton thanks to the purchase of Bruker F.T.I.R. system (using funds derived from the Science and Engineering Research Council) and the design, construction and development of new sample cell systems. The latest, sophisticated technology has improved the quality of the spectra avilable and hence the rigour in the analysis available. The subject has been reviewed recently:

A. Bewick, M. Kalaji, A.C.S. Summer Symp. Series 288 Cat. Charact. Sciences 550 1986 (20).

Thus, a successful study has been completed on hydrogen evolution over platinum where particular attention has been paid to the adsorbed intermediates.

R.J. Nichols and A. Bewick, J. Electroanal. Chem. (in press)

C. Polymer Processing and Properties

The Southampton group is continuing at high intensity its research into the structure and properties of solids produced by quenching melts of polyolefins. The consequent high supercooling levels (and hence low values of the crystallization temps.) causes these materials

to have 'odd' properties but, of course, properties typical of commercially processed products. It is worth emphasising in this report that all industrially processed polymers are quench-cooled from the melt. This programme has led to a long series of publications of which only the most recent are reviewed here. Further work has been concentrated on the processes that occur during plastic deformation wherein it has been demonstrated that very few chains rupture during the re-organization of spherulitic materials into fibrillar species but that chains do rupture when oriented fibrillar material is itself further deformed by stretching.

P.J. Hendra, C. Hammond, B. Lator and H.A. Willis, Polymer 1988 29, 49-53.

and

P.J. Hendra, A.J. Peacock and H.A. Willis, Polymer 1987, 28, 705.

and

C. Passingham, P.J. Hendra, M.E.A. Cudby , V. Zichy, Polymer 5-68 1988 (in press).

A bye product of this research has been an interest in the structure of flowing polymer melts. Flowing melts have been examined by X-ray diffraction.

M.A. Taylor, P.J. Hendra and H.A. Willis. J. Pol. Sci. Pal Letts, 1986, 24, 83.

by infrared and Raman methods (See earlier report and Ph.D. Thesis Southampton L. Hanna 1988) from which it is clear that little or no orientation is to be found in a sheared melt. The origin at the molecular level of die swell thus become obscure and is the subject of study at this time.

The techniques required to make optical measurements in hostile environments such as those described above have been extensively develope. In particular, the use of optical fibres in Raman spectroscopy has been highly fruitful and the technology is now at the stage that it can be used routinely.

P.J. Hendra, G. Ellis and D. Cutter, J. Raman Spectroscopy (in press).

Vibrational spectroscopy supported by NMR measurements have been applied for some years to a variety of problems in polymer analysis, the latest outcome being an investigation into the molecular level structure of linear-low-density polyethylenes and the role this structure plays in controlling the properties of some crystalline solids produced from their melts.

P.J. Hendra, A.J. Peacock and H.A. Willis, Polymer 1988 (in press).

The importance of the ONR support to the relatively small polymer group is perhaps indicated best by the fact that at the time this report is being written, no less than two postgraduate enjoying whole or partial support for the contract have been successfully examined for their Ph.D. degrees with the last 12 months. Much of the work in the theses will be further progressed and reported in future progress reports.

Very recently, preliminary work was completed on the development of Fourier Transform Raman methods and this has been mentioned in earlier sections. The method is under intensive development at Southampton in collaboration with the Perkin Elmer Company who delivered an early prototype spectrometer to Southampton early in August 1988. Little of this work was prepared for publication during the report period but a whole series of paper has been produced immediately after September 1987. Again, the O.N.R. funding was crucial in that it permitted the Raman group to undertake speculative preliminary work when it was most opertune (during the winter of 1986-1987).

D. CONCLUSION

A very considerable number of publications have been produced as a result of the research funded under this contact. The funds have also been used to support a large number of postgraduate students with most beneficial results. Further, the very preliminary work on the development and exploitation of Fourier Transform Raman methods made possible by the O.N.R. support has led (under a new contact) to an incredibly rapid development of the method and the construction and refinement of probably the most sophisticated and highest performance Fourier Transform Spectrometers currently in existance.